

(12) UK Patent Application (19) GB (11) 2 170 799 A

(43) Application published 13 Aug 1986

(21) Application No 8603421

(22) Date of filing 12 Feb 1986

(30) Priority data

(31) 60/026001	(32) 13 Feb 1985	(33) JP
60/156670	16 Jul 1985	
60/252301	11 Nov 1985	

(71) Applicant
Seiko Epson Corporation (Japan),
4-1 2-choime Nishishinjuku, Shinjuku-ku, Tokyo, Japan

(72) Inventors
Nobutaka Matsuo,
Yoshitaka Itoh,
Sadao Kanbe,
Haruo Osafune,
Masanobu Motoki

(74) Agent and/or Address for Service
J. Miller & Co., Lincoln House, 296-302 High Holborn,
London WC1V 7JH

(51) INT CL⁴
C03C 1/02 3/04 3/06

(52) Domestic classification (Edition H):
C1M 400 401 CC

(56) Documents cited
None

(58) Field of search
C1M
Selected US specifications from IPC sub-class C03C

(54) Method of preparing silica glass

(57) A method of preparing silica glass comprises the steps of: preparing a first solution which contains particulate silica obtained by hydrolyzing an alkyl silicate with a basic reagent, preparing a second solution by hydrolyzing an alkyl silicate with an acid reagent, mixing said first and said second solutions at a predetermined mixing ratio to obtain a sol solution, gelling said sol solution to form a wet gel, drying said wet gel to form a dry gel, and sintering said dry gel to obtain silica glass.

SPECIFICATION

Method of preparing silica glass

- 5 This invention relates to a method for preparing silica glass. 5
 Various suggestions have been made for preparing a silica glass by the sol-gel method, e.g. by Nogami, Nakatani et al., Journal of Non-Crystalline Solids, 37,191, 1980; Ravinovich et al., Journal of Non-Crystalline Solids, 47,435, 1982; and Toki et al; British Patent Application No. 84/18301. In the method of Toki et al., the pH of a sol solution of a metal alkoxide hydrolyzed solution, in which fine particle silica is uniformly dispersed, is adjusted to a value in the range of 3 to 6 and the porous dry gel which is obtained is sintered. As a result, a large piece of silica glass (for example, 15cm in width, 15cm in length and 0.5cm in thickness) which cannot be attained by the other two methods is prepared with a good yield. Thus Toki et al's method is the best of the above three methods. 10
- 10 However, in the method of Toki et al., the silica glass obtained by sintering is likely to contain impurities such as metal ions, crystals, foams, and irregularly shaped foreign particles. If the silica glass is required to be of high quality, as will be the case if it is employed as a silica substrate for a photo-mask or as a preform of an optical fibre, the glass formed by the method of Toki et al may not be of adequate quality. 15
- 15 It is therefore an object of the present invention to provide a method for preparing silica glass of uniform form and high quality which is free from impurities such as metal ions, crystals, foams and irregularly shaped foreign particles. 20
- 20 Although, therefore, the present invention is primarily directed to any novel integer of step, or combination of integers or steps, as herein disclosed, nevertheless according to one particular aspect of the present invention, to which, however, the invention is in no way restricted, there is provided a method of preparing silica glass comprising the steps of preparing a first solution which contains particulate silica obtained by hydrolyzing an alkyl silicate with a basic reagent, preparing a second solution by hydrolyzing an alkyl silicate with an acid reagent, mixing said first and said second solutions at a predetermined mixing ratio to obtain a sol solution, gelling said sol solution to form a wet gel, drying said wet gel to form a dry gel, and sintering said dry gel to obtain silica glass. 25
- 25 In the present invention, a liquid material of high purity can be selected as a starting material and so high-quality silica glass can be produced which does not have impurities such as metal ions, debris, dust and other foreign particles. 30
- 30 Preferably, pores in the dry gel are closed. This may be effected in an He atmosphere or under reduced pressure. Alternatively, the pores may be closed under reduced pressure after processing in an He atmosphere. 35
- 35 Before closing pores in the dry gel, the dry gel may be subjected to a treatment comprising removing an OH group and/or removing chlorine or fluorine.
 The pores may, moreover, be closed by heating the dry gel to a temperature between 900 and 1400°C at a heating rate of between 30 and 400° per hour.
- 40 Preferably the sol solution is introduced into a container prior to being gelled therein. 40
 The main particle diameter of the said particulate silica is preferably between 0.01 and 1.0 microns. Moreover, the first and second solutions may be mixed in the ratio of between 20 to 80 and 85 to 15 in terms of the molar ratio of the silica included in the first and second solutions respectively. Furthermore, the sol solution may be gelled after its pH has been adjusted to a value of at least 3.0. The features mentioned in this paragraph assist in producing a porous dry gel which is unlikely to be fractured during the sintering step. 45
- 45 Preferably, the amount of particulate silica in the said first solution is at least 0.05 g/ml. Moreover, it is preferable that the amount of effective silica in the sol solution is at least 0.1g/ml. The features mentioned in this paragraph assist in the formation of a wet gel composition which is unlikely to be fractured during the drying step. 50
- 50 The wet gel is preferably dried by heating the wet gel to a temperature of between 50 and 160°C at a heating rate of 120°C per hour. This assists in the formation of a dry gel having a good yield (i.e. a large number of acceptable articles).
- 55 The sintering of the dry gel preferably comprises removing absorbed water therefrom. Thus the absorbed water may be removed by heating the dry gel to a predetermined temperature of between 20 and 400°C at a heating rate of not more than 400°C per hour. Moreover, the dry gel is preferably maintained at the predetermined temperature for at least an hour. 55
- 60 The sintering of the dry gel also preferably comprises removing carbon therefrom. Thus the carbon may be removed by heating the dry gel to a temperature of between 400 and 900°C at a heating rate of between 30 and 400°C per hour. 60
- 65 The sintering of the dry gel also preferably comprises promoting a dehydrating condensation reaction. This reaction may be promoted by heating the dry gel to a temperature of between 900 and 1300°C at a heating rate of between 1 and 400°C per hour. Preferably, the dry gel is maintained at the last-mentioned temperature for at least 30 minutes.
- 65 The pores of the dry gel may be closed by heating the dry gel to a temperature in the range of 900 to 65

1400°C at a heating rate of between 30 and 400°C per hour. Moreover, the dry gel may be maintained at the last-mentioned temperature for at least 1 hour.

The dry gel is preferably made vitreous by heating the dry gel to a predetermined temperature and maintaining it at this temperature for a predetermined length of time.

5 The features mentioned in the preceding five paragraphs assist in the formation of a transparent glass with a good yield. 5

By using the features described above, a high-quality silica glass can be produced which contains far less in the way of impurities such as metal ions, crystals, foams and other irregularly shaped foreign particles in comparison with the glass produced by the conventional methods.

10 Moreover, by closing the pores as described above, the foams and irregularly shaped foreign particles included in the so-obtained glass are further reduced. Thus such closing of the pores assists in eliminating small foams of a diameter of less than 1 micron and assists in eliminating spaces caused by foreign particles which are likely to be produced when making the dry gel vitreous. In this way, an extremely high quality silica glass can be obtained which is to be used for purposes such as a silica substrate for a photo-mask. 10

15 Furthermore, by combining the following features with the above-mentioned features, an extremely high quality silica glass and a preform of an optical fibre may be prepared with a good and stable yield: 15

(1) The materials of the first and the second solutions should be of high-purity and the small amount of dust and foreign particles should be eliminated by distillation, filtration (e.g. in a filter whose holes are of a diameter of not more than 0.2 microns) and so on. 20

(2) The steps before the casting of the sol solution into the container should be performed at a cleanliness not less than class 3000 and preferably of class 100. 20

Preferably, the first solution is subjected to a centrifugal force of between 50 and 10,000 G, and the obtained supernatant liquid and the second solution are mixed together.

25 Preferably also the first solution is filtered at least once with a filter having a fineness of not more than 50 microns, and the resulting filtrate and the second solution are mixed together. Moreover, the said second solution may have been filtered at least once with a filter having a fineness of not more than 50 microns. 25

The sol solution may be filtered at least once with a filter having a fineness of not more than 50 microns. 30

The sol solution may be subjected prior to gelation to a reduced pressure.

The sol solution may be gelled while subjecting it to a centrifugal force of between 50 and 500G.

The hydrolysis of the second solution may be effected while adding at least 20% alcohol by weight with respect to the alkyl silicate.

35 The container preferably has openings which collectively comprise not more than 10% of the surface area of the container. 35

The wet gel is preferably allowed to shrink prior to the start of the drying. Thus the wet gel is preferably allowed to shrink by at least 8% in length prior to the start of the drying.

The sol solution is preferably maintained in the container at a temperature of between 10 and 50°C.

40 The inner surface of the container which is in contact with the sol solution may be of hydrophobic material. 40

The sintered silica glass produced is preferably transparent.

Before closing the pores in the gel, the steps of removing any OH group and of removing chlorine or fluoride may be effected.

45 The invention also comprises a silica glass member when made by the method described above. Such a glass member may be a plate, or may be cylindrical or may be tubular. 45

The invention is illustrated by the following Examples.

Example 1

1. Preparing the first solution

50 704.8g of refined commercially available ethyl silicate, 3766ml of anhydrous ethanol, 225.9ml of ammonia water (29%) and 243.8g of water were mixed and the mixture was violently stirred for 2 hours. Then the resulting solution was maintained still in a cool, dark place overnight to grow fine particle silica. The solution was condensed under the reduced pressure to 560ml and the pH thereof was adjusted to 4.5 by 55 using 2 normal hydrochloric acid to yield the first solution. 55

The first solution included 203.9g of silica particles whose mean particle diameter was 0.14 micron. (The calculated amount of silica in the first solution was about 0.33g/ml).

2. Preparing the second solution

60 199.5g of 0.02 normal hydrochloric acid was added to 576.6g of refined commercially available ethyl silicate and the mixture was violently stirred to carry out the hydrolysis, and thus the second solution was obtained. 60

3. Preparing the sol solution and gelation

The first and second solutions formed as above were mixed and the pH of the mixture was adjusted to 4.7 by using 0.2 normal ammonia water and water and the volume thereof was adjusted to 1600ml to yield the sol solution. (The concentration of effective silica in the sol solution was 0.231g/ml).

- 5 The sol solution was cast into ten polypropylene containers (of 400mm width, 400mm length and 100mm height) by pouring and each container was sealed with a lid. In 45 minutes from the time when the pH was adjusted, the sol was gelled and a wet gel was obtained. 5

4. Drying

- 10 The wet gels formed in the manner described above were aged for 2 days while being maintained in the sealed containers. Then the lid of each container was replaced by another lid formed with apertures which covered 0.4% of the surface area of the lid, and the wet gel was then dried at 60°C. In 14 days, 9 dry gels which were not fractured even at the room temperature were obtained with a yield of 90%. 10

5. Sintering

- 15 The 9 dry gels were placed in a sintering oven and were heated from 30°C to 200°C at a heating rate at 30°C per hour, were maintained at 200°C for 5 hours, were heated from 200°C to 300°C at a heating rate of 30°C per hour, and were maintained at 300°C for 5 hours to remove the absorbed water. 15

- 20 Then the gels were further heated from 300°C to 1050°C at a heating rate of 30°C per hour and were maintained at 1050°C for 30 minutes to remove carbon and ammonium chloride and to promote a dehydrating condensation reaction. 20

- 25 The gels were then heated at 1250°C at a heating rate of 30°C per hour and were maintained at 1250°C for 30 minutes to close the pores in the gels and were then heated to 1400°C at a heating rate of 60°C per hour, and were maintained at 1400°C for 1 hour to remove the pores. As a result, 9 transparent silica glass members were obtained with a yield of 100%. 25

- By polishing opposite sides of the silica glass members so obtained, silica glass plates of 18cm width, 18cm length and 2mm thickness were obtained.

- 30 It was found that, in preparing the second solution, if the hydrolysis was carried out while adding at least 20% alcohol by weight with respect to the alkyl silicate, the reaction progressed more uniformly and accordingly the viscosity of the obtained second solution and consequently of the sol solution was lowered, so that the handling of the sol solution was facilitated. However, in this case, the transparent glass member which is obtained is a little smaller and so whether this feature is used or not will depend upon the cost. 30

Example II

- 35 In order to assess the conditions required for making a silica glass member of the same size as those of Example 1 with a good yield, the various experiments were conducted and the results are shown in Table 1 below. From the results of these experiments, the following features are shown to be desirable:- 35

- 40 1) The mean particle diameter of the fine particle silica included in the first solution should desirably be between 0.01 and 1.0 micron. 40

- 2) The concentration of the fine particle silica included in the first solution should desirably be 0.5g/ml or higher.

- 3) The first and the second solutions should desirably be mixed in the ratio of between 20 and 80 to 20 in terms of the molar ratio of included silicon atoms.

- 45 4) The concentration of the effective silica content in the sol solution should desirably be 0.10g/ml or more. 45

- 5) The sol solution should desirably be gelled after adjusting the pH of the sol solution to a predetermined value of at least 3.

- 6) The wet gel should desirably be dried in a container covered with a lid having openings constituting not more than 10% of the surface area of the lid. 50

- 7) The wet gel should desirably be dried by heating it from 40°C to a predetermined temperature between 50 and 160°C at a heating rate of not more than 120°C per hour.

- 8) The dry gel should desirably be sintered to form a transparent glass member by the following 5 processes:

- 55 (i) removing absorbed water 55
(ii) removing carbon
(iii) promoting a dehydrating condensation reaction
(iv) closing the pores in the gel
(v) making the gel vitreous.

- 60 9) The absorbed water should desirably be removed by heating the dry gel to a predetermined temperature between 20 and 400°C at a heating rate of not more than 400°C per hour and, if necessary, maintaining it at this temperature for at least 1 hour. 60

- 10) Carbon should desirably be removed by heating the dry gel to a predetermined temperature between 400 and 900°C at a heating rate of between 30 and 400°C per hour.

- 65 11) The dehydrating condensation reaction should desirably be promoted by heating the dry gel to a 65

predetermined temperature between 900 and 1300°C at a heating rate between 1 and 400°C per hour and, if necessary, maintaining it at this temperature for at least 30 minutes.

12) The pores should desirably be closed by heating the dry gel to a predetermined temperature between 900 and 1400°C at a heating rate of between 30 and 400°C per hour and, if necessary, maintaining the dry gel at this temperature for at least 1 hour.

13) The dry gel should desirably be made vitreous by heating the dry gel to a predetermined temperature and maintaining it at this temperature for a predetermined period of time.

TABLE 1

No	$\bar{\alpha}$ (μm)	C_1 (g/ml)	$1/1+2$ (%)	C_2 (g/ml)	pH	opening ratio(X)	drying condition	sintering condition	field after drying (X)	yield after sintering(X)
1	0.005	0.20	55	0.15	4.7	0.4	*	*	0	—
2	0.05	0.28	55	0.231	4.7	0.4	*	*	80	100
3	0.14	0.32	55	0.231	4.7	0.4	*	*	90	100
4	0.33	0.33	55	0.231	4.7	0.4	*	*	100	100
5	1.5	0.35	55	0.231	4.7	0.4	*	*	30	67
6	0.14	0.45	55	—	—	—	—	—	Particles separated out during condensation	
7	0.14	0.05	55	0.10	5.0	0.4	*	*	20	0

TABLE 1 CONTD

No	$\bar{\alpha}$ (μm)	C_1 (g/ml)	$1/1+2$ (%)	C_2 (g/ml)	pH	opening ratio(X)	drying condition	sintering condition	field after drying (X)	yield after sintering(X)
8	0.14	0.32	80	0.231	4.7	0.4	*	*	50	80
9	0.14	0.32	20	0.231	4.7	0.4	*	*	0	—
10	0.14	0.32	55	0.1	5.5	0.4	*	*	20	0
11	0.14	0.32	55	0.18	5.0	0.4	*	*	60	83
12	0.14	0.32	55	0.231	3.0	0.4	*	*	More than 1 week is required for gelation— economically undesirable. 20	
13	0.14	0.32	55	0.231	4.7	10	*	*	0	—
14	0.14	0.32	55	0.231	4.7	0.4	* *	* *	0 ~ 100	0 ~ 100

$\bar{\alpha}$ is the mean particle diameter of fine particle silica included in the first solution.

C_1 is the concentration of fine particle silica included in the first solution,

$1/1+2$ is the molar number of the silicon included in the first solution with respect to the molar number of the silicon included in the first and second solutions,

5 C_2 is the concentration of effective silica in the sol solution

pH is the pH of the sol solution

Opening ratio is the ratio rate of the total area of the openings in the lid with respect to the surface area of the lid

* The drying conditions and the sintering conditions were the same as in Example I,

10 ** Various conditions were examined.

Example III

In order to assess the conditions required for obtaining an extremely high-quality silica glass member, various experiments were conducted and the results are shown in Table 2 below. From the results, it is proved to be preferable to employ some or all of the following conditions for economic reasons:-

15 1) The pores in the dry gel may be closed by one of the following three methods:

(i) The pores are closed in an He atmosphere

(ii) The pores are closed under reduced pressure.

(iii) The pores are closed under reduced pressure after processing in an He atmosphere.

20 2) The first and the second solutions as the starting materials should desirably be of high-purity and small amounts of debris and foreign particles should desirably be removed by distillation or filtration.

3) The processes employed until the sol solution is cast into a predetermined container should desirably be performed with a cleanliness of not more than class 3000 and preferably not more than class 100.

25 4) After applying centrifugal force between 50 and 10000G to the first solution, the obtained supernatant liquid and the second solution should be mixed.

5) After filtering the solution at least once using a filter having a fineness not more than 50 micron, the obtained supernatant liquid and the second solution should be mixed.

6) After filtering the second solution at least once using a filter having a fineness not more than 50 microns, the obtained filtrate and the first solution should be mixed.

30 7) The sol solution should desirably be filtered at least once using a filter having a fineness not more than 50 microns.

8) Before the gelation, the sol solution should desirably be processed at least once under reduced pressure.

9) The sol solution should desirably be cast into a predetermined container and gelled while applying a centrifugal force of between 50 and 500G.

10) Before closing the pores in the gel, a step of removing an OH group and a step of removing chlorine or a step of removing fluorine should preferably be included.

TABLE 2

No	Pores closing	Material refining	Cleanliness	Centrifugal #1	Filter #2			Reduced pressure #3 (sol)	Centrifugal #4 (sol)	Crystals	Pores larger than 1 μ m #5	Irregularly shaped foreign particles larger than 1 μ m #6	Foams & foreign particles smaller than 1 μ m #7	Total evaluation #8
					1st	2nd	sol							
1	in the air	O	class 3000	O	0.4	0.2	1 μ	O	O	O	Δ	O	X	D
2	He	O	class 3000	O	0.4	0.2	1 μ	X	X	O	O	O	O	B
3	reduced pressure	O	class 3000	O	0.4	0.2	1 μ	X	X	O	O	O	O	B
4	He + reduced pressure	O	class 3000	O	0.4	0.2	1 μ	X	X	O	O	O	O	B
5	He	X	class 3000	O	0.4	0.2	1 μ	X	X	Δ	O	Δ	X	C
6	He	O	X	O	0.4	0.2	1 μ	X	X	O	O	O	X	C
7	He	O	class 100	O	0.4	0.2	1 μ	X	X	O	O	O	O	A
8	He	O	class 3000	O	0.4	0.2	X	X	X	O	O	O	O	B
9	He	O	class 3000	X	0.4	0.2	1 μ	X	X	O	O	O	Δ	B

TABLE 2 (CONTD)

5	No	Pore closing	Material refining	Densification	Centrifugal #1	Filter #2			Reduced pressure #3(sol)	Centrifugal #4(sol)	Crystals	Foams larger than 1 μ m #5	Irregularly shaped foreign particles larger than 1 μ m #6	Foams & foreign particles smaller than 1 μ m #6	Total evaluation #7	5	
						1st	2nd	sol									
	10	He	O	class 3000	O	X	0.2	1 μ	X	X	O	O	O	Δ	B		
10	11	He	O	class 3000	O	0.4	X	1 μ	X	X	O	O	O	Δ	B	10	
	12	He	O	class 3000	O	X	X	1 μ	X	X	O	O	O	Δ	B		
	13	He	O	class 3000	O	X	X	X	X	X	O	O	Δ	Δ	C		
15	14	He	O	X	O	X	X	X	X	O	O	O	Δ	X	C	15	
	15	He	O	class 3000	O	0.4	0.2	1 μ	O	X	O	O	O	\odot	A		
	16	He	O	class 3000	O	0.4	0.2	1 μ	X	O	O	O	O	\odot	A		
20	17	He	O	class 3000	O	0.4	0.2	1 μ	O	O	O	O	O	\odot	A	20	
	18	He	O	class 3000	O	0.4	0.2	1 μ	O	X	O	O	O	\odot	A		
25																	25
	*1	1000G 1 hour O . . processed X . . unprocessed															
	*2	pore diameter of final filter (membrane type)															
		X . . unprocessed															
30	*3	50mmHg 2 minutes O . . processed X . . unprocessed														30	
	*4	200 G about 45 minutes O . . processed															
		X . . unprocessed															
	*5	number of foreign particles per 1 inch square:-															
		O (O ~ 1), Δ (1 ~ 10), X(> 10).															
35	*6	The light of a condenser lamp was shone onto the container and its scattering was observed by the naked eye.														35	
40	©	. . nothing was seen														O . . almost nothing was seen	40
	Δ	. . a flickering was seen														X . . seemed hazy	
	*7	A . . excellent quality														B . . extremely high quality	
	C	. . high quality														D . . normal	
	*8	After removing OH group, and removing chlorine, pores were closed.															
45																	45

In this embodiment, the detailed experimental conditions are omitted from description. However, the same conditions as in Example I are used.

50 The step of removing the OH group and the step of removing chlorine and fluoroine are performed as follows:

After promoting the dehydrating condensation reaction in the same way as in Example I, the gel was cooled down to 700°C and maintained for 30 minutes while a gas consisting of a mixture of 2 l/min of He and 0.2 of Cl₂ was passed over it. Then the gel was heated at 800°C at a heating rate of 60°C per hour while He gas only was passed over it, the gel was maintained at 800°C for 1 hour while a gas consisting of a mixture of 2l/min of He and 0.2l/min of Cl₂ was passed over it, the gel was further heated at 900°C at a heating rate of 60°C per hour while He gas only was passed over it, and the gel was maintained at 900°C for 1 hour while a gas consisting of a mixture of 2l/min of He and 0.2l/min of Cl₂ was passed over it, thus removing any OH group. Then, by heating the gel to 1000°C at a heating rate of 60°C per hour while a gas consisting of a mixture of HE and O₂ in a ratio of 2l/min to 0.4l/min was passed over it, the gel being maintained at 1000°C for 1 hour, chlorine was removed.

It is clear that the present invention is applicable not only to the production of a pure silica glass member but also to a silica glass member including dopant such as Ti.

Example IV

1. Preparation of the first solution

1678.0 grams of ethyl silicate, 3585 mili-litres of unhydrated ethanol, 109 mili-litres of 29% ammonia water and 580.6 grams of water were mixed and the mixture was violently stirred. Then the solution was maintained still in a cool, dark place for one night to age the silica particles included therein.

After condensing the resulting solution under reduced pressure, the alcohol in the condensed solution was substituted by water in order to improve the yield in the subsequent drying step. The pH of the solution was adjusted to 4.0 by the addition of 2 normal hydrochloric acid in order to prevent abrupt gelation at the time when the solution would be mixed with the hydrolyzed solution. The resulting solution was filtered by a membrane filter as fine as 0.6 microns to obtain a silica dispersed solution containing silica particles whose mean particle diameter was 0.18 microns.

This solution is referred to as the first solution.

2. Preparation of the second solution

950.0 grams of 0.02 normal hydrochloric acid was added to 1372.9 grams of ethyl silicate and the solution was violently stirred to make the second solution.

3. Preparation of the sol solution and the gelation thereof

The first and the second solutions were mixed together and the pH of the mixture solution was adjusted to 4.69 by adding 0.2 normal ammonia water and water and the volume thereof was adjusted to 4000ml to obtain the sol solution. (The effective silica concentration of this sol solution was 0.220g/ml.).

The sol solution was cast to a depth of 2000mm into a cylindrical container of 50mm inner diameter and 2100mm height. After eliminating air for 2 minutes under a pressure of 50 torr, the container was covered by a lid and sealed. Gelation occurred 40 minutes after the pH of the sol solution was adjusted and a wet gel was obtained.

The above steps 1, 2 and 3 were performed in a clean room whose cleanliness was of class 100. Furthermore, the ethyl silicate, ethanol and water employed had been refined by distillation, and the hydrochloric acid and ammonia water employed included extremely little in the way of metal ion impurities, the latter having been filtered off by a membrane filter as fine as 0.2 microns.

4. Drying

10 wet gels obtained as above were aged in sealed containers for 3 days and then each gel was moved into a respective rotatable container having openings constituting 0.2% of the surface area. Each wet gel was dried at 60°C as the rotatable container was rotated at a rotational speed of 0.1 rotations per minute. In 17 days, 9 dry gels were obtained which were stable enough so that no fracture occurred even at room temperature. Thus the yield was 90%. The volume density of the obtained dry gel was 0.72g/cm³.

Then the 9 dry gels obtained as above were placed in a sintering oven and heated to 200°C at a heating rate of 30°C per hour, maintained at 200°C for 5 hours, were further heated to 300°C at a heating rate of 30°C per hour and were maintained at 300°C for 5 hours to remove the absorbed water. The gels were heated from 300°C to 920°C at a heating rate of 60°C per hour and were maintained at 920°C for 2 hours to remove carbon and ammonium chloride and to accelerate the dehydration condensation reaction. The gels were then cooled down to 800°C and were maintained at 800°C for 30 minutes while Cl₂ was passed over them at 0.2 litres per minute and He was passed over them at 2 litres per minute, the gels then being heated to 900°C at a heating rate of 60°C per hour, maintained at 900°C for 1 hour, heated to 1000°C at a heating rate of 60°C per hour and maintained at 1000°C for 3 hours to remove any OH group. Then with O₂ gas flowing over them, at 1 litre per minute, the gels were heated to 1100°C at a heating rate of 60°C per hour and were maintained at 1100°C for 30 hours to remove chlorine. Thereafter with only He gas being passed over them, the gels were heated to 1250°C at a heating rate of 30°C per hour and were maintained at 1250°C for 30 minutes to close the pores in the gels. The gels were then heated to 1450°C at a heating rate of 60°C per hour and were maintained at 1450°C for 1 hour, as a result of which the gels became non-porous. Thus 9 cylindrical transparent glass members were obtained with a yield of 100%.

The dimensions of each glass member so obtained was 23.2mm outer diameter and 928mm length, its weight being 862g. The yield of the material was almost 100%.

The obtained transparent glass was perceived to be of uniform quality and of the sufficient clarity when observed by the naked eye.

Moreover, by drawing the transparent glass so obtained and using a fluoric polymer as a cladding, more than 10km of optical fibre of 200 microns in core diameter and 300 micron in the diameter of the cladding was obtained for every one transparent glass member. The transmission loss of the optical fibre was less than 4dB/km at a wavelength of 0.85 microns and thus this optical fibre was demonstrated to be satisfactory in quality as an optical fiber for LAN.

Furthermore, the transparent glass of this Example has a very good light transmission property in itself and so may be used as a light transmission silica bar of a diameter from some hundred microns to some centimeters as it is or as a Q fibre. Such a light transmission silica bar can be used for illuminating a farm in a space station or an under-water ranch.

Example V

A sol solution, which was prepared as in Example IV, was gelled by rotating a gelling means and a tubular wet gel of 50mm outer diameter, 25mm inner diameter and 2000mm length was obtained. 10 wet gels were dried and sintered by following the same steps as in Example IV and then 10 transparent glass members were obtained with a yield of 100%.

The transparent glass member so obtained was of 23.2mm outer diameter, 11.6mm inner diameter and 928mm length.

By drawing the transparent glass member so obtained and by using a fluoric polymer as a cladding, more than 8km of an optical fiber of 200 microns core diameter and 300 microns diameter of cladding was obtained per glass member. The transmission loss of the optical fibre so obtained was 4dB/km at a wavelength of 0.85 microns and thus the optical fibre obtained was demonstrated to be used as an optical fibre for LAN.

Moreover, since the transparent glass member so obtained is tubular, it is suitable for a support tube for MCVD, a jacket tube of the preform used in the VAD method or the MCVD method, or a cladding tube used in the rod-in-tube method.

Particularly, since the transparent glass so obtained includes very little water (less than 100ppb), such a transparent glass can be used for producing an extremely high-quality optical fibre.

Example VI

A sol solution prepared as in Example IV was introduced to a depth of 80mm into a Teflon (Registered Trade Mark) container of 200mm square \times 100mm inner dimension and then gelled. By drying and sintering the gel so obtained at a ratio slower than in Example IV, a silica glass of 92mm square \times 37mm thickness was obtained.

Since this silica glass passes ultraviolet and visible light well and even passes light of a wavelength of 200nm, such a silica glass can be employed as a photomask used in the manufacture of an ultra-scale-integrated circuit of more than 1Mbit.

Furthermore, because the silica glass of this Example was thick, the glass could be made into a lens or prism. The lens obtained could be used in the manufacture of 256Kbit SRAM.

*Example VII**1. Preparation of the first solution*

Ethyl silicate, ethanol and water all refined by distillation, and guaranteed commercially available 29% ammonia water were filtered by a membrane filter having holes whose diameter was 0.2 microns and were mixed to form the compositions shown in Table 1. After being violently stirred for 4 hours, each solution was maintained still in a cool and dark place for one night to grow fine particle silica. Each solution was condensed and its pH was adjusted, and it was then filtered by a membrane filter having holes whose diameter was 10 microns. The resulting solution was referred to as the first solution.

<i>The first solution</i>	<i>A</i>	<i>B</i>	<i>C</i>
Ethyl silicate	44.1 litres	44.1 litres	41.1 litres
Ethanol	67.2 litres	67.2 litres	67.2 litres
Water	16.0 litres	15.6 litres	15.0 litres
Ammonia water	0.8 litres	1.2 litres	1.8 litres

The mean particle diameters of the fine particle silica included in the resulting first solutions A, B and C were 0.15 microns, 0.25 microns and 0.40 microns, respectively.

2. Preparation of the second solution

6.15 litres of 0.02 normal hydrochloric acid filtered by a membrane filter having holes whose diameter was 0.2 microns was added to 18.9 litres of ethyl silicate refined by distillation, and the mixed solution was violently stirred for carrying out the hydrolyzation. The resulting solution was referred to as the second solution. In this Example, three second solutions were prepared.

3. Preparation of the sol solution

The first solution A and one of the second solutions were mixed and the solution was filtered by a membrane filter having holes whose diameter was 0.8 microns. The solution was referred to as the sol solution A.

Similarly, the first solution B and one of the remaining second solutions were mixed and the mixture was filtered by a membrane filter having holes whose diameter was 2.0 microns. The solution was referred to as the sol solution B.

Similarly, the first solution C and the remaining second solution were mixed and the mixture was filtered by a membrane filter having holes whose diameter was 3.0 microns. The resulting solution was referred to as the sol solution C.

The pH and the liquid temperature of the sol solutions obtained as above were 4.5 and 20°C, respectively.

4. Gelation and drying

- 5 900-milli-litres of the sol solution A was cast into 50 containers (300mm square × 100mm height in inner diameter) and, after sealing the containers with lids, the sol solution A was gelled to yield 50 wet gels. 5
In the same way as above, 50 wet gels were formed respectively of the sol solutions B and C.
Then the so-obtained 150 wet gels in the sealed containers were aged at 30°C for 3 days and thereafter the lids of the containers were replaced by other lids having openings constituting 0.4% of the surface area of the lids, and the gels were dried therein at 65°C. In 14 days, dry gels were obtained which did not fracture even in the atmosphere and which had the yield shown by Table 4. 10

TABLE 4

15	<i>Sol solution used</i>	<i>Yield (%)</i>	15
	Sol solution A	62	
	Sol solution B	78	
20	Sol solution C	84	20

5. Sintering

- 25 The three kinds of dry gels obtained above were placed in a sintering oven in groups of 10 and were heated from 30°C to 200°C at a heating rate of 60°C per hour and were maintained at 200°C for 5 hours. 25
Then the gels were further heated from 200°C to 300°C at a heating rate of 60°C per hour and were maintained at 300°C for 5 hours to remove the absorbed water.
The gels were heated from 300°C to 700°C at a heating rate of 60°C per hour, were maintained at 700°C for 20 hours, and were then heated from 700°C to 900°C at a heating rate of 60°C, maintained at 900°C for 10 hours, further heated from 900°C to 1000°C at a heating rate of 60°C and maintained at 1000°C for 10 hours to remove carbon and ammonium chloride and to accelerate the dehydration condensation reaction. 30
While He gas was flowing into the sintering oven, the temperature was raised to 1200°C at a heating rate of 60°C and the gels were maintained at 1200°C for 2 hours to close the pores in the gels.
35 Further, the gels were heated to 1300°C at a heating rate of 60°C per hour and maintained at 1300°C for 1 hour. Then the gels became non-porous and 30 transparent glass members were obtained with a yield of 100%. 35
By polishing opposite surfaces of each of the resulting silica glass members, silica glass plates of 152mm square × 3mm thickness were obtained.
40 The silica glass of this Example included no observable foreign particles and was proved to be of extremely high quality. Moreover, the spectral characteristics of the glass over the ultra violet and visible range were flat. Accordingly, the obtained silica glass was of satisfactory quality for the photomask substrate used in manufacture of integrated circuits. 40

45 Example VIII

- 10 of each of three kinds of the dry gels obtained in the above Example VII (30 in all) were sintered by following the sintering programme specified below. 45
The gels were heated from 30°C to 200°C at a heating rate of 30°C per hour, were maintained at 200°C for 5 hours, and were then heated from 200°C to 300°C at a heating rate of 30°C per hour and were maintained for 300°C for 5 hours to remove absorbed water. 50
Next, the gels were heated from 300°C to 700°C at a heating rate of 30°C per hour, were maintained at 700°C for 20 hours, were heated from 700°C to 900°C at a heating rate of 30°C and were maintained at 900°C for 10 hours to remove carbon and ammonium chloride and to accelerate the dehydration condensation reaction. 55
Then the gels were cooled down to 700°C and were maintained for 30 minutes while subjected to a flow of He at the rate of 20 litres per minute and of Cl₂ at the rate of 2 litres per minute. The gels were heated to 1000°C at a heating rate of 30°C per hour and were maintained at 1000°C for 5 hours to remove any OH groups. 55
While subjected to a flow of O₂ gas at the rate of 20 litres per minute, the gels were maintained at 1000°C for 1 hour and were heated to 1100°C at a heating rate of 60°C per hour, and were maintained at 1100°C for 20 hours to remove chlorine. 60
While subjected to a flow of He gas at the rate of 20 litres per minute, the gels were maintained at 1100°C for 1 hour and thereafter heated to 1200°C at a heating rate of 30°C per hour, maintained at 1200°C for 10 hours, further heated to 1250°C at a heating rate of 30°C per hour and maintained at 1250°C for 10 hours to close the pores in the gels. 65

The temperature was raised to 1400°C at a heating rate of 60°C per hour and was maintained at 1400°C for 1 hour. Then the gels became non-porous and 30 transparent glass members were obtained with a yield of 100%.

By polishing opposite surfaces of the glass members, silica glass plates of 152 mm square x 3mm thickness were obtained.

No foreign particles were observed in the silica glass plates of this Example and so the silica glass was proved to be of high quality. Additionally, the spectral characteristics of the glass over the ultra violet and visible range were flat and suitable for use as the photomask substrate used in the manufacture of integrated circuits. Moreover, any OH group included in the glass was less than 1ppm and the glass was guaranteed to be transparent over a wide range from ultra violet to infrared. Accordingly, the glass produced has a quality which is satisfactory for use as a cell for various kinds of chemical, biological, physical and optical experiments.

CLAIMS

1. A method of preparing silica glass comprising the steps of: preparing a first solution which contains particulate silica obtained by hydrolyzing an alkyl silicate with a basic reagent, preparing a second solution by hydrolyzing an alkyl silicate with an acid reagent, mixing said first and said second solutions at a predetermined mixing ratio to obtain a sol solution, gelling said sol solution to form a wet gel, drying said wet gel to form a dry gel, and sintering said dry gel to obtain silica glass.
2. A method as claimed in claim 1 comprising closing pores in the dry gel.
3. A method as claimed in claim 2 in which the closing of pores in the dry gel is effected in an He atmosphere.
4. A method claimed in claim 2 in which the closing of pores in the dry gel is effected under reduced pressure.
5. A method as claimed in claim 2 in which the closing of pores in the dry gel is effected under reduced pressure after processing in an He atmosphere.
6. A method as claimed in any of claims 2 to 5 in which, before closing pores in the dry gel, the dry gel is subjected to a treatment comprising removing an OH group and/or removing chlorine or fluorine.
7. A method as claimed in any of claims 2-6 in which the pores are closed by heating the dry gel to a temperature between 900 and 1400°C at a heating rate of between 30 and 400°C per hour.
8. A method as claimed in any preceding claim in which the sol solution is introduced into a container prior to being gelled therein.
9. A method as claimed in any preceding claim in which the mean particle diameter of the said particulate silica is between 0.01 and 1.0 microns.
10. A method as claimed in any preceding claim in which the first and second solutions are mixed in the ratio of between 20 and 80 and 85 to 15 in terms of the molar ratio of the silica included in the first and second solutions respectively.
11. A method as claimed in any preceding claim in which the sol solution is gelled after its pH has been adjusted to a value of at least 3.0.
12. A method as claimed in any preceding claim in which the amount of particulate silica in the said first solution is at least 0.05g/ml.
13. A method as claimed in any preceding claim in which the amount of effective silica in the sol solution is at least 0.1g/ml.
14. A method as claimed in any preceding claim in which the wet gel is dried by heating the wet gel to a temperature of between 50 and 160°C at a heating rate of 120°C per hour.
15. A method as claimed in any preceding claim in which the sintering of the dry gel comprises removing absorbed water therefrom.
16. A method as claimed in claim 15 in which the absorbed water is removed by heating the dry gel to a predetermined temperature of between 20 and 400°C at a heating rate of not more than 400°C per hour.
17. A method as claimed in claim 16 in which the dry gel is maintained at the predetermined temperature for at least an hour.
18. A method as claimed in any preceding claim in which the sintering of the dry gel comprises removing carbon therefrom.
19. A method as claimed in claim 18 in which carbon is removed by heating the dry gel to a temperature of between 400 and 900°C at a heating rate of between 30 and 400°C per hour.
20. A method as claimed in any preceding claim in which the sintering of the dry gel comprises promoting a dehydrating condensation reaction.
21. A method as claimed in claim 20 in which the dehydrating condensation reaction is promoted by heating the dry gel to a temperature of between 900 and 1300°C at a heating rate of between 1 and 400°C per hour.
22. A method as claimed in claim 21 in which the dry gel is maintained at the last-mentioned temperature for at least 30 minutes.

23. A method as claimed in any preceding claim in which the dry gel is made vitreous by heating the dry gel to a predetermined temperature and maintaining it at this temperature for a predetermined length of time.
24. A method as claimed in any preceding claim in which the first solution is subjected to a centrifugal force of between 50 and 10,000 G, and the obtained supernatant liquid and the second solution are mixed together. 5
25. A method as claimed in any preceding claim in which the first solution is filtered at least once with a filter having a fineness of not more than 50 microns, and the resulting filtrate and the second solution are mixed together.
26. A method as claimed in claim 25 in which the said second solution has been filtered at least once with a filter having a fineness of not more than 50 microns. 10
27. A method as claimed in any preceding claim in which the sol solution is filtered at least once with a filter having a fineness of not more than 50 microns.
28. A method as claimed in any preceding claim in which the sol solution is subjected prior to gelation to a reduced pressure. 15
29. A method as claimed in claim 8 or in any claim appendant thereto in which the sol solution is gelled while subjecting it to a centrifugal force of between 50 and 500G.
30. A method as claimed in any preceding claim in which the hydrolysis of the second solution is effected while adding at least 20% alcohol by weight with respect to the alkyl silicate.
31. A method as claimed in claim 8 or in any claim appendant thereto in which the container has openings which collectively comprise not more than 10% of the surface area of the container. 20
32. A method as claimed in any preceding claim in which the pores of the dry gel are closed by heating the dry gel to a temperature in the range of 900 to 1400°C at a heating rate of between 30 and 400°C per hour.
33. A method as claimed in claim 32 in which the dry gel is maintained at the last-mentioned temperature for at least 1 hour. 25
34. A method as claimed in any preceding claim in which the wet gel is allowed to shrink prior to the start of the drying.
35. A method as claimed in claim 34 in which the wet gel is allowed to shrink by at least 8% in length prior to the start of the drying. 30
36. A method as claimed in claim 8 or in any claim appendant thereto in which the sol solution is maintained in the container at a temperature of between 10 and 50°C.
37. A method as claimed in claim 8 or in any claim appendant thereto in which the inner surface of the container which is in contact with the sol solution is of hydrophobic material.
38. A method as claimed in any preceding claim in which the sintered silica glass produced is transparent. 35
39. A method of preparing silica glass substantially as hereinbefore described with reference to any of the Examples.
40. A silica glass member when produced by the method claimed in any preceding claim.
41. A silica glass member as claimed in claim 39 in which the member is a plate. 40
42. A silica glass member as claimed in claim 39 in which the member is cylindrical.
43. A silica glass member as claimed in claim 39 in which the member is tubular.
44. Any novel integer or step, or combination of integers or steps, hereinbefore described and/or shown in the accompanying drawings irrespective of whether the present claim is within the scope of, or 45 relates to the same or a different invention from that of, the preceding claims. 45

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